Polarization dependent ARPES measurements of the valence band structure of anatase TiO$_2$

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Introduction
Titanium dioxide (TiO$_2$) has been widely used for the past two decades owing to its technologically promising properties. Regarding photocatalytic activities, anatase TiO$_2$ is superior to the rutile form. Although a large number of studies have been performed thus far, the fundamental properties of anatase such as the electronic structures of both valence and conduction band regions are less known than those of rutile. Anatase is commercially available in powder form. This is because of the difficulty to synthesize a large-scale single crystal anatase, owing to its less stable form in comparison with the rutile form. In the present study, we have fabricated epitaxial anatase thin films with a good crystallinity and elucidated the valence band structure of the thin films by angle-resolved photoemission spectroscopy (ARPES).

Experiment
Highly oriented anatase films with (001) orientation were epitaxially grown on LaAlO$_3$(100) with an in-plane relationship of [100]anatase//[010]LaAlO$_3$ using pulsed laser deposition with a KrF excimer laser. The ARPES measurements were performed at beam lines 1C and 11D of the Photon Factory, KEK. The valence band structure along the $\Gamma-Z$ axis was determined from normal emission spectra taken with various photon energies from 45 eV to 70 eV. The synchrotron radiation was linearly polarized in the incidence plane of the light.

Results and Discussion
The spectra were acquired with incidence angles of 20° and 55° (relative to the surface normal direction) so that the ratio of s- and p-polarized components was varied. The spectra were measured at both room temperature and liquid nitrogen temperature.

Fig. 1. Normal emission spectra of the anatase TiO$_2$ (001) surface measured by p-polarized (left) and s-polarized (right) synchrotron light.

Fig. 2. Valence band structure along the $\Gamma-Z$ axis of anatase TiO$_2$.

References